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Sol–gel derived coatings on glass

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Abstract

Sol–gel processing is a versatile method for depositing oxide based coatings on a variety of substrates in an economical manner. The present review will consider coatings deposited on glass, and will discuss a number of representative applications for such coatings, namely anti-reflection coatings, transparent conducting coatings, anti-static coatings, fluorinated coatings, coatings incorporating active dye molecules and ferroelectric coatings. © 1997 Published by Elsevier Science B.V.

1. Introduction

One of the key areas of application for sol–gel processing is that of coatings [1], where many perceived advantages over conventional methods have been claimed [2]. These include the ability to coat large, curved substrates in a cost effective method using simple deposition equipment [2], the ability to obtain coatings with high homogeneity and tailored inhomogeneity [1], low firing temperatures, and the ability to prepare materials which cannot be prepared by other methods (e.g., organic–inorganic hybrid materials) [3].

Sol–gel methods can be used to fabricate almost any single- or multi-component oxide coating. Such coatings have been deposited on glass to provide coloration [4], anti-reflection [5], selective reflection [6], electrochromism and photochromism [7], selective absorption [8], waveguiding [9], reduced friction [10], anti-soiling [10], reduced adhesion [10], transparent conductors [11], electro–optics [12], ferro-

electrics [12], sensors [13], and dye lasers [14]. For reasons of space, the present paper will consider anti-reflection and transparent conductors (where sol–gel processing competes against established commercial technologies), fluorinated coatings and coatings containing active dyes (where wet chemical processing has yielded novel materials), and ferroelectric films for optical applications (where the coatings represent vital elements of more complicated and expensive devices).

2. Anti-reflection (AR) coatings

AR coatings are one of the early applications of sol–gel methods [5,15]. Single, multi-layer and graded index AR coatings have been prepared by wet chemical methods [2]. In the first approach, a film is used with a refractive index n intermediate between the n s of the substrate and air, coupled with an optical path of $1/4\lambda$. Hence $n < 1.3$ is desired. Since the smallest n inorganic material, MgF_2 , has $n = 1.38$, porous or hybrid coatings are required. In the former case, the pore size should be smaller than λ and a homogeneous distribution of porosity is

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required to minimize scattering. Small n s are readily obtainable from porous sol–gel films [16–18].

Single-layer AR coatings are only effective at one λ ; but, using several layers increases the bandwidth over which low reflection losses can be obtained [19]. Multi-layer AR coatings deposited by sol–gel methods have been demonstrated on many substrates including glass [19]. An alternative method for obtaining broad band AR coatings uses a single coating with graded porosity, which results in a gradual change in n through the film, thereby minimizing reflection losses.

Sol–gel derived AR coatings have been prepared from both alkoxide and colloidal precursors. Colloid-based solutions have been widely investigated as precursors for porous coatings [20]; and such coatings have been extensively explored for high power optics [20–22]. Use of colloidal precursors has many advantages, including the ability to prepare many layers without cracking, low cost, excellent optical performance, high damage threshold and ease of application at room temperature on large substrates [23–25].

The abrasion resistance of colloid-based coatings can be increased by ammonia treatment or by incorporating a siloxane binder [26–28]. Thomas has prepared films with $1.22 \leq n \leq 1.44$ using solutions of colloidal SiO_2 + a polysiloxane [27–29]. The polysiloxane acts as both binder and filler for the colloidal particles. Increasing amounts of siloxane gave coatings of less porosity, increasing both n and abrasion resistance. Colloids have also been used to prepare highly reflecting coatings (reflectivities > 99%) for high power laser applications [29]. These coatings are based on oxides such as TiO_2 , AlOOH , ZrO_2 and HfO_2 [29]. Novel, $\lambda/4$, narrow bandwidth AR coatings using colloidal SiO_2 as the discontinuous phase and a perfluorinated organo-copolymer (Teflon AF 2400) as the continuous phase have $n = 1.30$ and high laser damage thresholds [30–32].

For graded index AR coatings, a porous layer is first deposited and then chemically etched [33,34]. The etchant produces a compositional gradient and hence a gradient in n . Chemical etching of multi-component gel films of SiO_2 – BaO and SiO_2 – B_2O_3 – Na_2O has been used to prepare films for high power applications with reflectivities in the range of 0.15 to 0.7% at $1.06 \mu\text{m}$ [33]. Coatings with graded n s have

been fabricated using a series of SiO_2 sols based on $\text{Si}(\text{OMe})_4$ aged for different times. This method has the potential of overcoming the problems of dealing with etchants [35,36].

Sol–gel derived AR coatings have been proposed for cathode ray tubes (CRTs) [37]. Graded- n structures have been prepared using layers in which the degree of cross-linking decreases from the substrate surface to the outer surface of the coating [38]. Coatings based on 2, 3 or 4 interference films have been deposited by alternately spin-coating solutions based on a Si alkoxide and higher- n solutions based on Ta, Ti or Zr [39].

Extensive use has been made of sol–gel solutions as vehicles/binders for colloidal particles [40]. AR light-scattering coatings have been prepared by spraying solutions of colloidal SiO_2 particles and a Si alkoxide [40]. These coatings are of similar quality to acid etched glass [40]. Alternatively, a large n Si alkoxide solution containing colloidal particles of Ta_2O_5 , TiO_2 , ZrO_2 or ZnS and a small n coating based on the same sol but containing MgF_2 particles can be alternately coated to produce AR coatings [41]. Low reflectivity films have also been prepared from sols based on MgF_2 , a Si alkoxide and a chelated Zr alkoxide [42], and also by dispersing MgF_2 particles (5 to 1000 nm) in a Si alkoxide based solution [43].

Anti-static/AR coatings have been prepared from a Si alkoxide solution containing fine In_2O_3 particles to form a transparent electrically conducting layer having high- n , followed by a Si alkoxide based solution to give a small n coating [44]. Similar coatings have also been prepared by dipping solutions of Sb-SnO_2 to give a multiparticle layer followed by a solution of SiO_2 particles in a $\text{Si}(\text{OEt})_4$ based solution to give a single particle low reflectivity coating [45]. A monolayer of SiO_2 particles in an alkoxide matrix deposited on a CRT has been used to prevent diffuse reflectance while giving high resolution and high contrast [45].

Films with a fine surface roughness ($< 0.01 \mu\text{m}$) have also been used for reducing the reflectivity of CRTs [46]. These were obtained using two $\text{Si}(\text{OEt})_4$ -based sols with different molecular weights. On firing, numerous micro-pits were formed. Such films are useful as a base or interlayer in multilayer stacks on glass. Coatings with controlled roughness

to reduce specular reflection were prepared by spraying alkoxide solutions (e.g., $\text{SiO}_2\text{--TiO}_2$) on glass surfaces [47]. Glare reducing coatings have also been made by using a Li stabilized silica sol [48].

Sol-gel processing is thus attractive for preparing AR coatings, and are used commercially in applications from high power lasers to CRTs. Such processing provides the ability to obtain porous films, films with tailored *ns* and films containing nanophase particles.

3. Transparent conducting and anti-static coatings

Transparent, electrically conducting oxide films are technologically important [49,50]. The most important techniques for preparing these films are magnetron sputtering for tin-doped indium oxide (ITO) [51] and CVD for fluorine-doped tin oxide [52]. Sol-gel processing has been investigated for preparing transparent conducting oxides. Undoped SnO_2 films derived from alkoxides are highly resistive, likely reflecting their highly stoichiometric character, with few oxygen vacancies [53]. Zr and Ti-doped SnO_2 coatings have also been deposited on glass by sol-gel methods [54].

Sb-doped SnO_2 has been prepared from ethoxide precursors derived from $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and SbCl_3 [55]. Such films have been prepared from precursors such as Sn and Sb butoxides. Surface resistances of about $200 \Omega/\square$ (resistivities of about 10^{-2} ohm cm) were obtained [56]. The best conductivity was obtained for doping levels of $\sim 7 \text{ wt\% Sb--SnO}_2$. Films have also been prepared using $\text{SnCl}_4/\text{SbCl}_3$ precursors, yielding resistivities of $1.2 \times 10^{-2} \text{ ohm cm}$ (7 mol% Sb) [57], and using a triethanolamine-alkoxide method [58]. In the latter work, the conductivity could be increased by first depositing a TiO_2 film on the glass. The films were less crystallized, but denser and more uniform than CVD deposited films. Sb- SnO_2 coatings have also been deposited on Nextel and E-glass cloths using Sn(IV) isopropoxide and Sb butoxide [59]. A doping of 7 mol% Sb was optimum. After coating 5 times and firing at 650°C for 5 h, the cloths had a sheet resistance of $18 \Omega/\square$. Sol-gel derived SnO_2 coatings on glass have also been investigated as sensors, e.g., for EtOH [60–62].

In addition to Sb-doped SnO_2 , sol-gel processing has been used to prepare ITO [11,63,64] and Cd stannate [65], and to deposit anti-static films on CRTs [66–69]. Coatings prepared from fine ITO powder ($0.2 \mu\text{m}$), a metal alkoxide and a phosphate-based coupling agent and dried at less than 200°C gave a surface resistivity of $1 \times 10^5 \Omega/\square$ [70]. ZnO based coatings from Zn acetate and Al or Zr alkoxide have also been explored for this purpose [71]. Coatings based on conductive microparticles, a Ti chelate and Si alkoxide could be cured at low temperature or by ultra-violet (UV) light [72]. Coatings based on Sb-doped SnO_2 sols and a Zr alkoxide gave a surface resistivity of $5 \times 10^8 \Omega/\square$ after firing at 250°C [73], as have conductive coatings based on Sn, Sb, In alkoxides and Si alkoxides [74].

Sol-gel processing is thus feasible for synthesizing transparent conductive coatings. Most work has been on preparing Sb-doped SnO_2 films, whereas F is the standard commercial dopant for SnO_2 [75]. Anion doping is, however, not trivial with sol-gel processing. Additionally, the benefits of low processing temperatures are not available here. Sol-gel derived conductive oxide films are typically fired at low temperatures which result in small grain sizes. This leads to larger scattering, which decreases the conductivity. The films require higher firing temperatures to increase the grain size and obtain higher conductivity. When the transparent conductor is deposited as the top electrode on devices, the required firing temperatures can impair the underlying materials. Further, sol-gel methods are not conformal, and this is a disadvantage for some device structures.

4. Fluorinated coatings

Fluorinated silane based coatings have been investigated for their hydrophobic and oleophobic properties. Applications such as lubricating treatments, adhesion control, textile treatments and a variety of low-soiling coatings have been explored [76], as have water repellent films for automotive windshields [77–82]. Glass substrates have been coated with solutions based on $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{Si}(\text{OMe})_3$ and $\text{Si}(\text{OEt})_4$ precursors. The coatings exhibited H_2O contact angles as large as 110° [83]. Glass coated with 3-glycidoxypentyl-trimethoxysilane,

$\text{Me}_2\text{Si}(\text{OEt})_2$, a fluorinated alkoxy silane and colloidal SiO_2 has a H_2O contact angle of 104° [77]. Similar contact angles have been obtained from $\text{Si}(\text{OEt})_4$ and $\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{Si}(\text{OMe})_3$ [78]. Coatings based on a boron alkoxide and a fluoroalkoxy silane have been explored [84], as have hydrophobic coatings obtained by first depositing an undercoat film with fine surface roughness ($0.01\text{ }\mu\text{m}$) followed by a fluoroalkoxy silane based coating [81], and soil proofing coatings based on $\text{Si}(\text{OEt})_4$, a Ti alkoxide and $\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{Si}(\text{OMe})_3$ [85].

Coatings with surface energies of 18 mJ/m^2 have been obtained from solutions containing fluorinated silanes with a matrix of $\text{Si}(\text{OEt})_4$ and $\text{MeSi}(\text{OEt})_3$ [10]. The coatings could withstand 500 000 wiper cycles under wet conditions without significant decreases in the surface energy [10]. The abrasion resistance of these coatings was increased by incorporation of ZrO_2 or SiO_2 nanoparticles [10]. The coatings also had a dust repellent effect. By modification of the solution chemistry, UV curable coatings based on a matrix of 3-trimethoxysilylpropylmethacrylate, $\text{Zr}(\text{O}^n\text{Pr})_4$ and methacrylic acid were produced [86]. The resulting contact angles became invariant when the fluorinated silane reached a concentration $\geq 1\%$, due to enrichment of the fluorinated chains at the air/film interface [86]. The smaller concentration of fluorinated chains at the substrate/film interface results in good adhesion of the film. H_2O contact angles approaching 118° were obtained [86].

Fluorinated alkoxy and chlorosilanes have been investigated for monolayer surface treatments, e.g., for the treatment of polarizer plates for liquid crystal displays [87], ultrahydrophobic surfaces [88], hydrophobic-oleophobic coatings for use in aircraft [89] and non-wettable glass [90].

Fluorinated sol-gel coatings illustrate the potential benefits of wet chemical processing for making novel materials, as small surface energy in a hard, abrasion-resistant film with good adhesive properties to a substrate. Many applications can be readily envisaged.

5. Dye composites

Numerous organic dyes have been incorporated into active sol-gel coatings on glass substrates. Due

to space limitations, we will consider only sensors, photochromism and lasers. Low temperature processing, high optical transparency, thermal stability, chemical inertness, and control of the molecular environment of the dye can be provided.

The highly porous nature of xerogel coatings makes them attractive for sensing [3]. Many dyes have been incorporated within such pores for sensing species such as cations, anions, gas molecules, protons and small organic molecules [91]. The sensing dye typically exhibits a change in fluorescence induced by changes in its molecular environment [13]. Two attractive dyes for pH sensors are fluorescein [13,92–95] and Coumarin 4 [96], which change chemical form with change in pH. The sensors usually have a matrix derived from $\text{Si}(\text{OEt})_4$. Leaching of the dye from the matrix can be reduced by treating the xerogel with a silane coupling agent [92] and can be eliminated by covalently bonding the dye to the host using a functionalized dye [14,97].

Sensors using dye doped sol-gel coatings on optical fibers have been prepared by removing the cladding on an optical fiber and re-coating it with a porous dye-doped xerogel on guiding excitation light through the fiber, the sensing dye is photo-excited by the evanescent wave [13,95,98,99]. The resulting fluorescence is coupled into a waveguide and can be read by a detector. Such devices have been developed with fluorescein for pH sensors [13,95] and with a Ru complex for O_2 sensors [98,99]. Response times as fast as 2–5 s have been reported, with a detection limit less than $1\% \text{ O}_2$ [99]. Compatibility with LEDs and photodiodes has been demonstrated [98–100].

To be viable commercially, sol-gel derived sensors require increased resistance to photobleaching, decreased temperature sensitivity, and increased selectivity. One approach [98] to reducing the effect of photobleaching on device performance uses a phase fluorometric method for detection as opposed to intensity based methods: In a Ru-doped xerogel, the fluorescence lifetime is a function of the O_2 concentration. By exciting with modulated light, the phase shift of the fluorescence can be measured. This shift is a strong function of the fluorescence lifetime and the modulation frequency [98].

There is much interest in developing a tunable solid-state laser. Most work on laser dyes in sol-gel

hosts has been on monoliths as gain media, but some have focused on waveguide coatings on glass. Lasing emission over most of the visible spectrum has been achieved with a variety of laser dyes [101–110] in hosts ranging from SiO_2 to $\text{SiO}_2\text{:TiO}_2$ inorganic–organic hybrids. The films often include Ti to provide the required large n s for waveguiding.

Lasing of red perylimide in sol–gel hosts synthesized from $\text{Ti}(\text{OEt})_4$ and 3-glycidylpropyltrimethoxysilane coated on glass has been demonstrated [107]. The guided fluorescence spectrum (max 630 nm) was red shifted compared to the bulk glass spectrum (max 607 nm), associated with reabsorption of the fluorescence light. Lasing in a waveguide has also been achieved in Rhodamine 6G and Coumarin 153 doped glasses derived from $\text{MeSi}(\text{OMe})_3$ [102]. A three layer waveguide was used, with the middle guiding layer composed of the dye-doped glass. The cladding layer was the same composition without the dye. With dye doping at large concentrations, the increase in n was enough to get guided light. The spectral properties of the guided light was again red shifted, and line narrowing was observed.

The main problem with laser dyes is the poor photostability of the dye upon long term exposure to high intensity light [110]. Work in our laboratory has determined the mechanisms of dye degradation and sought ways to improve photostability [110,112]. Covalently attaching the lasing dye to the sol–gel host, altering the processing and composition to remove porosity, controlling the acid or base environment of the dye, and using antioxidant additives have led to significant improvement in the photostability for coumarin and pyromethene dyes in xerogel films and SiO_2 –PDMS monoliths [111,112].

Photochromic (PC) materials have received attention. Useful PC materials have a large PC response (large absorption change), a large or small bleaching rate depending on whether the material is being used for switching or storage, and thermal and photochemical stability [7]. Spiropyrans are the most widely studied group of PC dyes. Here, the PC effect results from photo-induced isomerization, where the different forms of the dye have different absorption properties and where a heterolytic ring opening of the spiro C–O bond forms a zwitterionic merocyanine [113].

The first PC dye-doped sol–gel glass was reported in 1986 using a spiropyran (SP) dye (Aberchrome 670) [118]. Since then, both monoliths [114–120] and thin films have been prepared [7,121–123]. Due to the tendency of SP dyes to isomerize, they tend to be more sensitive to their molecular environment than other organic dyes. In a solvent host, the coloring rate for a SP dye is fast due to high dye mobility, but in a doped SiO_2 xerogel, the rate is decreased by a factor of 4 [117,120]. In an aged SiO_2 xerogel, the PC effect was completely diminished [117,120]. The increased rigidity and change in polarity of the environment around the dye hinders its intramolecular rotation, thus restricting or preventing isomerization [117,120]. Doping SPs in other sol–gel hosts has produced changes in PC properties [120]. Normal PC was observed with SP doped in a matrix derived from $\text{EtSi}(\text{OEt})_3$, while a reverse PC effect (decrease in absorption on exposure to light) was observed in a nanocomposite synthesized from $\text{Si}(\text{OMe})_4$ and PDMS [120]. The latter was attributed to diffusion of the dye to the silanol groups, forming the merocyanine form of the dye [116].

The kinetics of coloring can be controlled by tailoring the flexibility of the local cage of a PC dye. The molecular mobility of azobenzene dyes was less in sol–gel films compared to sol–gel monoliths and PMMA hosts [122,123]; while spirooxazine doped hybrid coatings exhibit faster color changes than the same dye in PMMA. The increased mobility was attributed to the presence of flexible glycidylpropyl groups [7]. In recent work, a silylated spirooxazine was covalently attached within hybrid coatings derived from $\text{EtSi}(\text{OEt})_3$ and 3-glycidylpropyltrimethoxysilane [124,125]. Silylation of the dye had little effect on the spectroscopic properties and PC intensity, but covalently attaching the spirooxazine decreased the bleaching rate.

An optical device utilizing a PC dye-doped sol–gel glass has been recently demonstrated, where the active material is coated between the ends of two optical fibers [121]. The PC material is colored or bleached by UV or visible light, respectively. When colored, optical signals will be attenuated. This device can be used as an optical power delay generator [121]. Although not the focus of present discussion, coatings based on AgCl particles in a sol–gel

$\text{SiO}_2\text{:B}_2\text{O}_3\text{:Al}_2\text{O}_3\text{:Na}_2\text{O}$ glass have shown PC behavior [116].

Overall, progress has been made in understanding dye-host interactions and their effects on lasing. A major limitation with the materials is photobleaching upon long-term light exposure, for which there may be design solutions, in part by novel device configurations and detection techniques. Improved photostability will depend upon synthesizing new active dyes with inherently higher photostabilities, and controlling the specific molecular interactions between the dye and host.

6. Ferroelectric films

Ferroelectric (FE) thin films have a wide range of technologically-important properties and are useful for a myriad of applications [126]. FE films typically have large n_s (> 2.0), and are suitable as waveguides. Traditional FE waveguides consist of bulk FEs with ion-exchanged, ion-implanted or diffused surfaces, e.g., bulk LiNbO_3 or strontium barium titanate (SBN). With large n_s , it is possible to use thin films (< 300 nm) as waveguides.

Optical losses in FE films may result from absorption (e.g., Ti^{3+} or oxygen vacancies), leakage, internal scattering (grain boundaries, domain walls), Rayleigh scattering from index inhomogeneities in the volume of the film and from interface/surface roughness [127] and Mie scattering from larger film defects, pores and inclusions. FE films for optical applications are often deposited on epitaxial single crystal substrates, but some are deposited on glass.

Waveguiding studies [112] of PLZT films have centered on a single composition, PLT 28. Even for the same nominal composition (PLT 28), a wide range of optical attenuations (1.4 to 15 dB/cm) has been reported. This range is due to the effects of microstructure, porosity and processing on optical properties [12]. FE films with cubic structures (e.g., BaTiO_3 fired at low temperatures or PLT 28) have small loss, with the loss increasing with increasing grain size and stronger anisotropy [12]. One benefit of sol-gel processing is the low processing temperatures which permit the use of glasses with T_g s (glass transition temperatures) less than that of fused silica. Such low processing temperatures have been ex-

ploited to yield films with small grain sizes (< 100 nm) on glass substrates which have the smallest reported loss (1.4 dB/cm) of any PLT 28 films (even epitaxial or single-crystal films) [12]. Dense, amorphous PZT films have been prepared which have losses of 1.1 dB/cm, comparable to that of single component paraelectric films [128]. Such films also have large n_s (2.0 to 2.4) and hence thin films (100 nm) can be used as passive waveguides.

The electro-optic (EO) coefficients of films, however deposited, are usually less than those of bulk samples. The smaller values for the films may be due to chemical interactions between film and substrate, porosity in the films, differences in phase distributions between film and bulk, and substrate clamping effects [129]. Typical EO coefficients for FE films (< 50 pm/V) are comparable to those of the best EO polymer films (55 pm/V) [130]. Recent work in our laboratories [131] has indicated that high linear EO coefficients (> 55 pm/V) can be obtained for polycrystalline PLZT films without the need for expensive single crystal substrates. Linear EO coefficients as large as 315 pm/V were obtained for sol-gel derived PZT 53/47 films [131]. This is the largest reported value for any sol-gel or sputtered PLZT film, and is larger than bulk LiNbO_3 and is near the bulk value for PZT. Large linear (81 pm/V) and quadratic (4.0×10^{-16} m²/V²) EO coefficients have been reported for sol-gel derived PZT 65/35 [132] and sputtered PLZT 9/35/65 (i.e., $\text{Pb}_{0.91}\text{La}_{0.09}(\text{Zr}_{0.35}\text{Ti}_{0.65})_{0.98}\text{O}_3$) [133], respectively. An intermediate layer of PLT can enhance the crystallinity of subsequently-deposited PLZT films, resulting in quadratic EO coefficients which are larger by a factor of 4 than if no PLT layer were present [133].

FE films containing nanoscale metal or semiconductor particles provide unique optical and electrical properties [134–140]. The optical properties of such colloid particles differ from those of bulk materials because the electrons and holes are confined to a small volume. With such quantum confined particles, the materials show increased responsiveness to photonic excitation. The third order optical susceptibility, χ^3 , is one measure of this non-linear-optic (NLO) effect, and materials with large values of χ^3 are desired for many applications.

Classical materials of this type consist of Au or

Pt-doped SiO_2 , but perovskite films containing colloidal Au particles have been reported [141–145], with Au-doped BaTiO_3 [141] films exhibiting χ^3 values larger by a factor of 10 than those of Au-doped SiO_2 [135]. Here the larger n matrix leads to higher optical activity as predicted by the Maxwell–Garnett equation [146]. Sol–gel processing is attractive for preparing perovskite films due to the low processing temperatures (resulting in small grain size (< 100 nm) films with small optical losses ($\alpha < 1$ dB/cm)) and controlled size (5 to 20 nm) of the colloids [147]. Results obtained in our laboratory indicate that the chemistries of the nanocolloids are important in determining the colloid size and the losses of the films [133].

For through-plane EO applications, the optical path length is small; and polycrystalline films can be utilized without substantial loss in performance. This is where sol–gel derived films offer advantages in large linear EO coefficients coupled with moderate optical losses. The use of polycrystalline films also reduces the need for expensive single crystal or epitaxial substrates, thus decreasing device costs.

Overall, the major advantage of sol–gel processing FE films is the low processing temperature which yields dense amorphous or small grain size (< 100 nm) films with small optical losses (< 1 dB/cm). However, a major problem is obtaining crystalline perovskite PLZT with large Zr content compositions; such compositions are preferred due to their inherently large quadratic EO coefficients. Due to the large optical losses in crystalline PLZT films with large grain sizes (< 100 nm), EO devices utilizing such films should be in a transmission mode for which the optical path is short. The large indices of these films provide large values of χ^3 coefficients. For χ^3 materials low processing temperatures are essential to obtain small matrix losses and to ensure small cluster size and size distribution of the nanocolloids. Alternative methods such as sputtering are unattractive due to homogeneity and stoichiometry problems.

7. Conclusions

Sol–gel processing has been investigated as a method for depositing coatings on glass. Early work

in this area began more than seven decades ago, but the last 15 years have seen a veritable explosion in interest in the area. It is feasible today to deposit almost any combination of oxides as films using appropriate precursor solutions. Extensive research has built a broad base of knowledge which is ripe for commercial development. It is expected that greatest commercial success will develop in areas where sol–gel processing yields coatings with unique combinations of properties rather than in areas where such processing must compete with established processes and offer only potential cost advantages.

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